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# CATALYTIC PYROLYSIS OF MIXTURES MODELING MUNICIPAL WASTE

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## Abstract

In this work the temperatures of the thermal decomposition of model waste mixtures were determined with and without catalysts under slow heating conditions applying thermogravimetry-mass spectrometry (TG/MS) technique. The catalytic effect of HZSM-5 and Ni-Mo catalysts were tested on the thermal stability of model waste mixtures. Significantly decreased thermal decomposition temperature (by about 200°C) was observed in case of plastic mixture in the presence of 10 % HZSM-5 catalyst. The catalytic effect of HZSM-5 catalyst was hindered when the domestic waste model mixtures contained biomass components as well. The effect of cellulose and lignin on the catalytic activity of HZSM-5 catalyst was tested and significant poisoning effect was observed in both cases. The presence of 50% cellulose or 10% lignin in the waste mixture completely deactivates the HZSM-5 catalyst.

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**Keywords:** catalytic pyrolysis, polymer, HZSM-5, domestic waste, TG/MS

## 1. Introduction

The increasing amount of domestic waste is one of the most serious environmental, social and economic issues of the modern society. The conversion of waste biomass and plastics into valuable feedstock by pyrolysis represents a promising way for recovering the organic content of the waste materials. The pyrolytic recycling can be more efficient by applying appropriate catalysts. The composition of the pyrolysis products can be more advantageous; and the pyrolysis temperature can be decreased which means energy saving for the pyrolytic process.

Thermal decomposition of a multicomponent mixture is always a complex issue, since chemical reactions could take place between the components or their decomposition products. Modified thermal stability and changed composition of the decomposition product can be observed [1]. Several catalysts have also been tested on the thermal decomposition of biomass or plastic wastes; however the catalytic co-pyrolysis of biomass and plastic waste is hardly studied. In an earlier study higher catalyst efficiency was found for municipal plastic waste than for biomass containing municipal solid waste using HZSM-5 or NiMo catalyst [2].

It is known that the main components of the municipal solid waste (MSW) are plastics, papers and other organic wastes (e.g. wood, leftover food, textile etc.). However polyethylene (PE) and polypropylene (PP) represent more than a half of the municipal plastic waste and polyethyleneterephthalate (PET) is also a significant component in spite of the selective waste collection system.

In this study, the catalytic thermal decomposition of synthetic polymer - biomass mixtures were examined under slow heating by thermogravimetry-mass spectrometry (TG/MS) technique. The catalytic activity of HZSM-5 and NiMo catalysts on the decomposition temperature of plastic and biomass-plastic model waste mixtures were studied.

## 2. Materials and Methods

### 2.1 Materials

The waste model mixtures were composed of PE, PP, PET, newspaper, paperboard and a piece of pinewood. Table 1 summarizes the composition of the studied waste model mixtures. The mixtures were cryo-ground in a Retsch MM301 mill, to obtain homogenous samples. Cellulose (Avicel) and beech milled wood lignin were applied as biomass components. The effects of the zeolite type HZSM-5 and Ni-Mo (on Al<sub>2</sub>O<sub>3</sub> support) catalysts were tested using 1:1 and 10:1 waste/catalyst ratios. The catalysts were mixed into the model mixtures in the appropriate ratios.

Table 1. Composition of the studied model waste mixtures

Name of model wastes	Plastic waste	Biomass waste	Domestic waste
Composition (m/m%)	PE 40% PP 40% PET 20%	newspaper 40% cardboard 40% pine sawdust 20%	PE 20% PP 20% PET 10% newspaper 20% cardboard 20% pine sawdust 10%

## 2.2 Methods

Thermogravimetry/mass spectrometry (TG/MS) measurements were performed on a modified Perkin-Elmer TGS-2 thermobalance and a Hiden HAL 2/301 PIC quadrupole mass spectrometer. Typically 0.5–4 mg pure or mixed sample was placed into the platinum sample pan and heated at a  $20^{\circ}\text{C min}^{-1}$  up to  $900^{\circ}\text{C}$  in argon atmosphere. A small proportion of the evolved gas and vapor was introduced into the mass spectrometer through a glass lined metal capillary transfer line heated to  $300^{\circ}\text{C}$ . The quadrupole mass spectrometer operated at 70 eV electron energy.

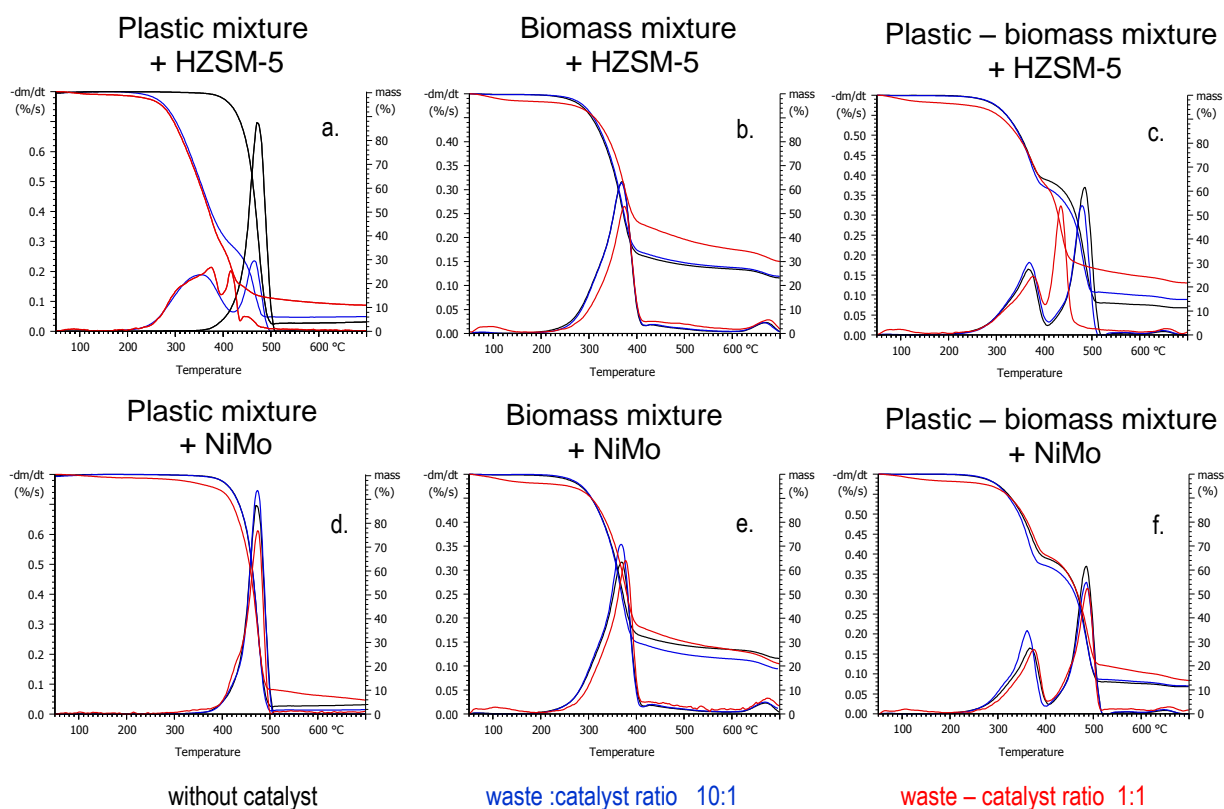


Figure 1. TG and DTG curves of waste mixtures without catalyst (black solid lines) and in the presence of HZSM-5 or NiMo catalyst in a ratios waste:catalyst = 10:1 (blue dashed lines) and waste:catalyst = 1:1 (red dotted lines).

## 3. Results and Discussion

### 3.1 Effect of catalyst on the thermal stability under slow heating rate

The thermal decomposition of the mixtures and the effect of the catalysts on the decomposition temperatures were studied by TG/MS technique. The TG and DTG curves in Figure 1 show the thermal decomposition of waste model mixtures in the presence of catalyst in two different ratios and without catalyst as well. The TG curves of the pure catalysts were subtracted from the TG curves of waste – catalyst mixtures in an appropriate ratio. Thus, each TG and DTG curve represents the weight loss and weight loss rate of the waste excluding the mass of the catalyst.

Figure 1a shows the thermal decomposition of plastic waste mixture both in the absence and presence of HZSM-5 catalyst. The PE-PP-PET mixture decomposes in a single step; the weight loss starts at around 380°C and reaches the maximal rate of decomposition at 470°C. In the presence of HZSM-5 the weight loss starts as low as 200°C. The reason of the intensive decrease in the starting temperature of decomposition is the strong cracking property of the HZSM-5 catalyst. Using both catalyst ratios of 1:1 and 10:1 the thermal stability of the plastic mixture decreases to the same extent; up to 360°C the DTG curves in the presence of catalyst are parallel. Using 10% catalyst the rate of polymer decomposition decreases above 360°C and about a quarter of the plastic mixture decomposes at higher temperatures. The second decomposition step takes place in the temperature range of the plastic waste decomposition without catalyst. Using the HZSM-5 catalyst in a 1:1 ratio almost the whole amount of plastic mixture decomposes below 450°C, however the shape of the DTG curve shows that the decomposition proceeds in several steps. The presence of 10% HZSM-5 catalyst slightly increases the amount of char, while using the catalyst in 1:1 ratio almost triplicates that.

According to Figure 1b the applied HZSM-5 catalyst does not modify the thermal stability of biomass waste mixture significantly; the shape of the TG and DTG curves and maximal rate of decomposition ( $DTG_{max}$ ) does not change noticeably. Using the catalyst in a 1:1 ratio a moderate increase in the amount of char was observed, while 10% catalyst does not have effect on the char yield.

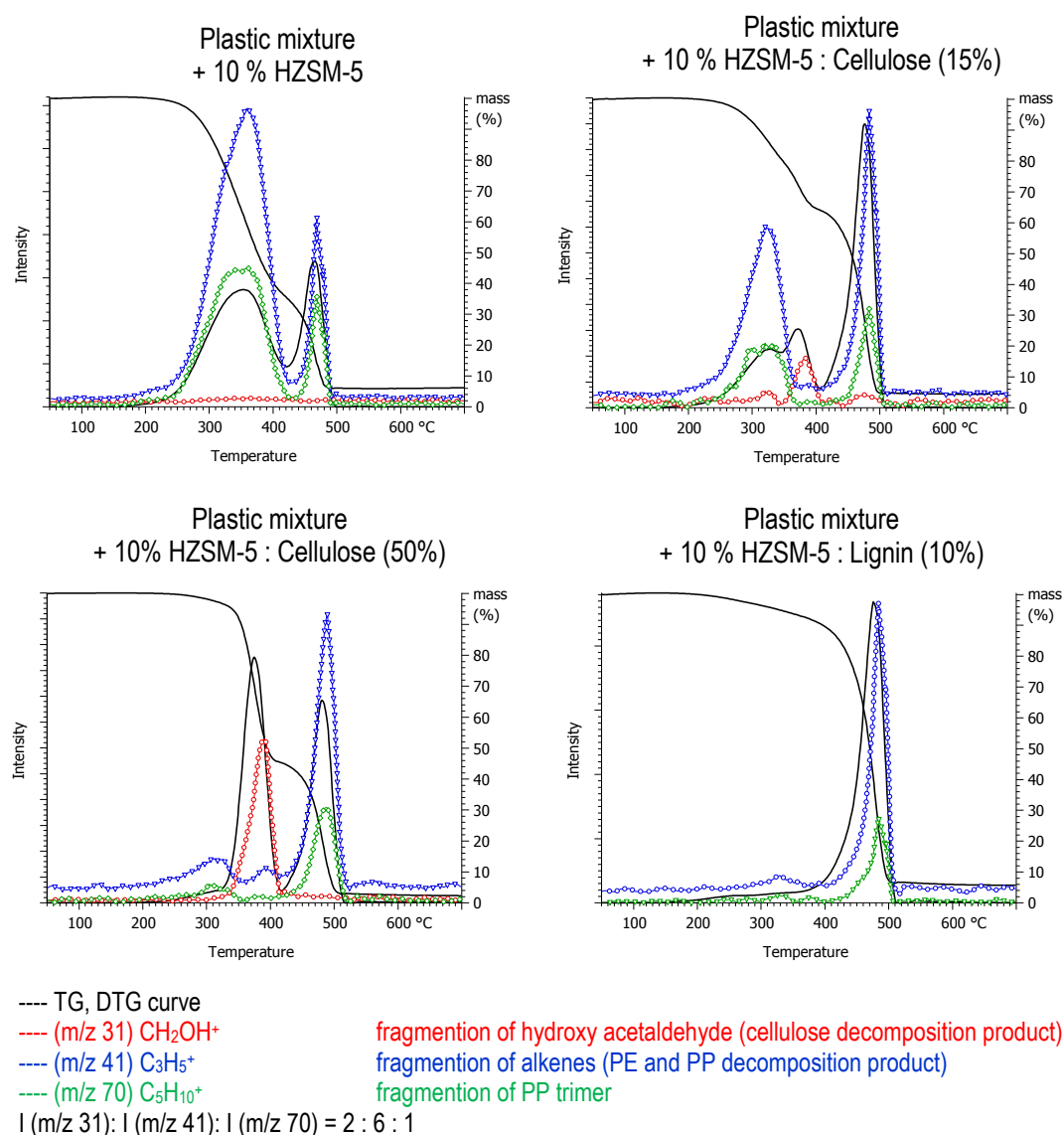


Figure 2. TG, DTG and ion intensity curves of 10% HZSM-5 catalyst containing plastic mixtures in the presence of cellulose and lignin.

The TG and DTG curves of plastic-biomass mixture in the absence and presence of HZSM-5 catalyst are presented in Figure 1c. This waste mixture decomposes in two well separated steps without catalyst. On the basis of the DTG curves of biomass and plastic mixtures (Figure 1a and b) the first decomposition step represents the decomposition of the biomass part of the mixture, while the second decomposition step with the DTG maxima at around 500°C stands for the decomposition of the plastic components in the mixture. As Figure 1c presents, the thermal stability does not change significantly in the presence of 10% HZSM-5 catalyst. However, the DTG maximum of the first decomposition step is slightly higher, whereas the intensity of second decomposition step is slightly lower. Using the catalyst in 1:1 ratio the effect of the catalyst is clearly visible. The first decomposition step takes place in the same temperature range than in the absence of catalyst indicating the unchanged thermal decomposition of the biomass. The second decomposition stage starts and reaches the maximal rate at about 70°C lower temperature in the presence of HZSM-5 catalyst in 1:1 ratio. The decomposition occurs in a narrow temperature range and is finished at around 470°C. Probably the whole amount of plastic waste decomposes thermally in this step, as there is no significant weight loss in the temperature range of decomposition of plastic mixture without catalyst.

Comparing to HZSM-5, the NiMo catalyst does not change the thermal stability of the analyzed waste mixtures to a high extent. However, the amount of char increases slightly in case of plastic and plastic-biomass mixtures applying the catalyst in 1:1 ratio.

### 3.2 Effect of biomass components on the catalytic effect of HZSM-5 catalyst

In order to understand the hindering effect of biomass on the efficiency of HZSM-5 catalyst, the thermal decomposition of polymer mixtures containing cellulose and lignin was studied. Figure 2 presents the TG, DTG and typical MS ion intensity curves of plastic mixtures containing 10% HZSM-5 catalyst and various amounts of cellulose and lignin. The ion curve at  $m/z$  41 ( $C_3H_5^+$ ), which is one of the most abundant MS fragment ion of alkenes, belongs to the thermal decomposition of PE and also to that of PP. The evolution of the main pyrolysis product of PP, namely propylene trimer can be monitored by its most intensive fragment ion ( $m/z$  70). Hydroxy acetaldehyde, measured at  $m/z$  31 fragment ion, is a typical cellulose decomposition product.

Figure 2a shows the evolution profile of alkenes and that of PP trimer from the plastic mixture in the presence of 10% HZSM-5 catalyst. As the curves demonstrate, both PE and PP decompose in the temperature range of 230-450°C during the catalytic pyrolysis process, while the plastic residue decomposing at higher temperatures seems to contain higher ratio of PP. Comparing these curves with the thermal decomposition of the plastic mixture containing 15% of cellulose (Figure 2b), the deactivating effect of the cellulose decomposition products on the cracking property of HZSM-5 is clearly visible. The catalytic pyrolysis of PE and PP starts at the same temperature (at around 230°C) than in the absence of cellulose, and their decomposition rate increases up to the point, when the cellulose content of the mixture starts to decompose (around 330°C). At this temperature the ion intensity curves of the thermal degradation products of PP and PE fall into their baseline indicating the interrupted decomposition of the plastics. The peak on the ion        intensity curve of  $m/z$  31 (peak maximum at 380°C) presents the thermal decomposition of cellulose. The remaining part of PE and PP decompose at around 500°C, in the temperature range of PE and PP decomposition without catalyst. Mixing 50% cellulose into the plastic mixture, the catalytic effect of 10% HZSM-5 is almost invisible, only a slight decrease in the TG curve and a short slope of the ion intensity curve at  $m/z$  41 below 330°C denote the thermal degradation of a small part of PE and PP at low temperature. The main part of the plastic components decomposes above 450°C.

Figure 2d presents the TG, DTG and ion intensity curves of plastic mixture containing 10% lignin besides the 10% HZSM-5 catalyst. As the curves shows, 10% lignin completely destroys the catalytic activity of HZSM-5. The thermal decomposition of the total amount of plastics proceeds at their decomposition temperature without catalyst. The reason could be that the lignin decomposes in a wide range of temperature starting at around 250°C.

## 4. Conclusions

The effect of HZSM-5 and NiMo catalysts on the thermal decomposition of model waste mixtures was studied applying TG/MS technique.

It was found that the thermal decomposition temperature decreased by about 200°C, when 10 % HZSM-5 catalyst was added to the plastic mixture. Nevertheless, in case of the domestic waste model mixtures, the catalytic effect of HZSM-5 catalyst was hindered to a great extent under slow heating. We studied the impact of biomass components on the catalytic effect of HZSM-5 and concluded that the decomposition products of both cellulose and lignin deactivate the HZSM-5 catalyst to a great extent. Adding 15% cellulose to the mixture eliminates the catalytic effect at the temperatures of cellulose decomposition. The presence of 10% lignin also destroys the catalytic activity of HZSM-5 on the thermal decomposition of the plastic components of waste mixtures.

The applied NiMo catalyst does not modify significantly the thermal stability of the studied model waste mixtures.

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## 5. Acknowledgement

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